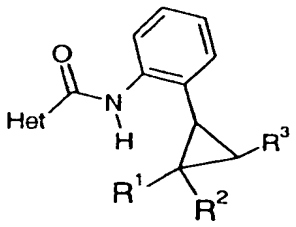
O-CYCLOPROPYL-CARBOXANILIDES AND THEIR USE AS FUNGICIDES

The present invention relates to novel ortho-substituted-cyclopropyl-azol-carboxamides which have microbiocidal activity, in particular fungicidal activity. The invention also relates to the preparation of these compounds, to novel intermediates used in the preparation of these compounds, to agrochemical compositions which comprise at least one of the novel compounds as active ingredient, to the preparation of the compositions mentioned and to the use of the active ingredients or compositions in agriculture or horticulture for controlling or preventing infestation of plants by phytopathogenic microorganisms, preferably fungi.

EP0545099A2, JP06220035 and JP02129171 disclose certain ortho-unsubstituted-cyclopropyl-azol-carboxamides

The present invention provides a compound of formula (I):



(I)

Het is a 5- or 6-membered heterocyclic ring containing one to three heteroatoms, each independently selected from oxygen, nitrogen and sulphur, the ring being substituted by groups R^4, R^5 and R^6; R^1 is hydrogen or halo; R^2 is hydrogen or halo; R^3 is optionally substituted C_{2-12} alkyl, optionally substituted C_{2-12} alkenyl, optionally substituted C_{2-12} alkynyl, optionally substituted C_{3-12} cycloalkyl, optionally substituted phenyl or optionally substituted heterocyclyl; and R^4, R^5 and R^6 are, independently, selected from hydrogen, halo, cyano, nitro, C_{1-4} alkyl, C_{1-4} haloalkyl, C_{1-4} alkoxy(C_{1-4})alkyl and C_{1-4} haloalkoxy(C_{1-4})alkyl, provided that at least one of R^4, R^5 and R^6 is not hydrogen.

Halo is fluoro, chloro or bromo.

Each alkyl moiety is a straight or branched chain and is, for example, methyl, ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl, *iso*-propyl, *n*-butyl, *sec*-butyl, *iso*-butyl, *tert*-butyl or *neo*-pentyl.

When present, each optional substituent on an alkyl moiety is, independently, selected from halo, hydroxy, cyano, C_{1-4}alkoxyC(=O), formyl, nitro, C_{1-4} alkoxy,

C_{1-4} haloalkoxy, C_{1-4} alkylthio, C_{1-4} haloalkylthio, HC(OR')=N and R'R''NN=C(H); where R' and R'' are, independently, hydrogen or C_{1-4} alkyl.

Alkenyl and alkynyl moieties can be in the form of straight or branched chains. The alkenyl moieties, where appropriate, can be of either the (E)- or (Z)-configuration. Examples are vinyl, allyl and propargyl.

When present, each optional substituent on alkenyl or on alkynyl is, independently, selected from those optional substituents given above for an alkyl moiety.

Cycloalkyl includes cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl.

When present, each optional substituent on cycloalkyl is, independently, selected from C_{1-3} alkyl and those optional substituents given above for an alkyl moiety.

The term heterocyclyl refers to a non-aromatic or aromatic ring containing up to 10 atoms including one or more (preferably one or two) heteroatoms selected, each independently, from O, S and N. Examples of such rings include 1,3-dioxolanyl, tetrahydrofuranyl, morpholinyl, thienyl and furyl.

When present, each optional substituent on phenyl or on heterocyclyl is, independently, selected from C_{1-6} alkyl and those optional substituents given above for an alkyl moiety. When present, there are up to four optional substituents on phenyl, each independently selected.

When present, each optional substituent on an alkyl moiety is, independently, selected from the preferred list of halo, hydroxy, methoxy, trifluoromethoxy, difluoromethoxy, cyano and nitro.

When present, each optional substituent on alkenyl or on alkynyl is, independently, selected from the preferred list of halo and cyano.

When present, each optional substituent on cycloalkyl is, independently, selected from the preferred list of methyl, ethyl, trifluoromethyl, methoxy, trifluoromethoxy and cyano.

When present, each optional substituent on phenyl or on a heterocyclyl group is, independently, selected from the preferred list of halo, hydroxy, methoxy, trifluoromethoxy, difluoromethoxy and cyano.

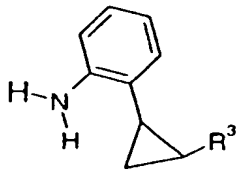
It is preferred that Het is pyrrolyl, pyrazolyl, thiazolyl, pyridinyl, pyrimidinyl, thiophenyl, furyl, isothiazolyl or isoxazolyl (more preferably pyrrolyl, pyrazolyl or thiazolyl), each being substituted by groups R^4, R^5 and R^6.

Preferably R^1 and R^2 are, independently, hydrogen or fluoro.

Preferably R^3 is C_{2-6} alkyl, optionally substituted C_{3-8} cycloalkyl, phenyl, thienyl or furyl.

Preferably R^4, R^5 and R^6 are, independently, selected from hydrogen, halogen, C_{1-4} alkyl, C_{1-4} haloalkyl and C_{1-4} alkoxy(C_{1-4})alkyl; provided that at least one of R^4, R^5 and R^6 is not hydrogen. More preferably R^4, R^5 and R^6 are, independently, selected from hydrogen, halogen, methyl, C_{1-2} haloalkyl and methoxymethyl; provided that at least one of R^4, R^5 and R^6 is not hydrogen.

Compounds of formula (II):



(II)

where R^3 is as defined above for a compound of formula (I), are also novel and are useful as intermediates in the preparation of compounds of formula (I).

Therefore, in another aspect the present invention provides a compound of formula (II) where R^3 is as defined above for a compound of formula (I).

The compounds of formula (I) and of formula (II) may exist as different geometric or optical isomers or in different tautomeric forms. This invention covers all such isomers and tautomers and mixtures thereof in all proportions as well as isotopic forms such as deuterated compounds.

The compounds in Tables 1 to 6 below illustrate compounds of the invention.

Table 1 provides 22 compounds of formula (II) wherein R^3 is as defined in Table 1.

Table 1

Compound Number	R^3
1.1	CH_2CH_3
1.2	$CH_2CH_2CH_3$
1.3	$CH(CH_3)_2$
1.4	$CH_2CH_2CH_2CH_3$
1.5	$CH_2CH(CH_3)_2$

1.6	$C(CH_3)_3$
1.7	$CH_2CH_2CH_2CH_2CH_3$
1.8	$CH_2CH_2CH(CH_3)_2$
1.9	$CH_2CH_2CH(CH_3)_2$
1.10	cyclopropyl
1.11	cyclobutyl
1.12	cyclopentyl
1.13	cyclohexyl
1.14	cycloheptyl
1.15	cyclooctyl
1.16	phenyl
1.17	p-Cl-phenyl
1.18	p-F-phenyl
1.19	p-Br-phenyl
1.20	thienyl
1.21	furyl
1.22	α-methylcyclopropyl

Table X represents Table 2 (when X is 2) and represents Table 3 (when X is 3).

Table X

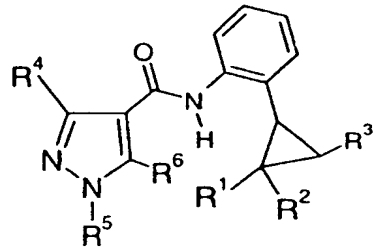
Compound Number	R^1	R^2	R^3	R^4	R^5	R^6
X.1	H	H	CH_2CH_3	CF_3	CH_3	H
X.2	H	H	CH_2CH_3	CF_3	CH_2OCH_3	H
X.3	H	H	$CH_2CH_2CH_3$	CF_3	CH_3	H
X.4	H	H	$CH_2CH_2CH_3$	CF_2H	CH_3	H
X.5	H	H	$CH(CH_3)_2$	CF_3	CH_3	H
X.6	H	H	$CH(CH_3)_2$	CF_2H	CH_3	H
X.7	H	H	$CH(CH_3)_2$	CFH_2	CH_3	H
X.8	H	H	$CH(CH_3)_2$	CH_3	CH_3	Cl
X.9	H	H	$CH(CH_3)_2$	CH_3	CH_2CH_3	Cl

Compound Number	R^1	R^2	R^3	R^4	R^5	R^6
X.10	H	H	$CH(CH_3)_2$	CH_3	CH_3	F
X.11	H	H	$CH(CH_3)_2$	CH_3	CH_2CH_3	F
X.12	H	H	$CH(CH_3)_2$	CF_2Cl	CH_3	F
X.13	H	H	$CH_2CH_2CH_2CH_3$	CF_3	CH_3	H
X.14	H	H	$CH_2CH_2CH_2CH_3$	CF_2H	CH_3	H
X.15	H	H	$CH_2CH_2CH_2CH_3$	CH_3	CH_3	F
X.16	H	H	$CH_2CH_2CH_2CH_3$	CH_3	CH_3	Cl
X.17	H	H	$CH_2CH(CH_3)_2$	CF_3	CH_3	H
X.18	H	H	$CH_2CH(CH_3)_2$	CF_2H	CH_3	H
X.19	H	H	$CH_2CH(CH_3)_2$	CFH_2	CH_3	H
X.20	H	H	$CH_2CH(CH_3)_2$	CF_3	CH_2OCH_3	H
X.21	H	H	$CH_2CH(CH_3)_2$	CH_3	CH_3	F
X.22	H	H	$CH_2CH(CH_3)_2$	CH_3	CH_3	Cl
X.23	H	H	$C(CH_3)_3$	CF_3	CH_3	H
X.24	H	H	$C(CH_3)_3$	CF_2H	CH_3	H
X.25	H	H	$C(CH_3)_3$	CF_2H	CH_3	H
X.26	H	H	$C(CH_3)_3$	CH_3	CH_3	F
X.27	H	H	$C(CH_3)_3$	CH_3	CH_3	Cl
X.28	H	H	$C(CH_3)_3$	CF_2Cl	CH_3	H
X.29	H	H	$CH_2CH_2CH_2CH_2CH_3$	CF_3	CH_3	H
X.30	H	H	$CH_2CH_2CH(CH_3)_2$	CF_3	CH_3	H
X.31	H	H	$CH_2CH_2CH(CH_3)_2$	CF_2H	CH_3	H
X.32	H	H	$CH_2CH_2CH_2CH_2CH_2CH_3$	CF_3	CH_3	H
X.33	H	H	cyclopropyl	CF_3	CH_3	H
X.34	H	H	cyclopropyl	CF_2H	CH_3	H
X.35	H	H	cyclopropyl	CH_3	CH_3	F
X.36	H	H	cyclopropyl	CH_3	CH_3	Cl
X.37	H	H	cyclobutyl	CF_3	CH_3	H
X.38	H	H	cyclobutyl	CF_2H	CH_3	H

Compound Number	R^1	R^2	R^3	R^4	R^5	R^6
X.39	H	H	cyclopentyl	CF_3	CH_3	H
X.40	H	H	cyclopentyl	CF_2H	CH_3	H
X.41	H	H	cyclopentyl	CFH_2	CH_3	H
X.42	H	H	cyclopentyl	CF_2Cl	CH_3	H
X.43	H	H	cyclopentyl	CH_3	CH_3	F
X.44	H	H	cyclopentyl	CH_3	CH_3	Cl
X.45	H	H	cyclohexyl	CF_3	CH_3	H
X.46	H	H	cyclohexyl	CF_2H	CH_3	H
X.47	H	H	cyclohexyl	CFH_2	CH_3	H
X.48	H	H	cyclohexyl	CF_2Cl	CH_3	H
X.49	F	F	cyclohexyl	CF_3	CH_3	H
X.50	H	H	cyclohexyl	CH_3	CH_3	F
X.51	H	H	cyclohexyl	CH_3	CH_3	Cl
X.52	H	H	cycloheptyl	CF_3	CH_3	H
X.53	H	H	cycloheptyl	CF_3	CH_2CH_3	H
X.54	H	H	cycloheptyl	CF_2H	CH_3	H
X.55	H	H	cycloheptyl	CFH_2	CH_3	H
X.56	H	H	cycloheptyl	CF_2Cl	CH_3	F
X.57	H	H	cycloheptyl	CH_3	CH_3	F
X.58	H	H	cycloheptyl	CH_3	CH_3	Cl
X.59	H	H	cyclooctyl	CF_3	CH_3	H
X.60	H	H	cyclooctyl	CF_2H	CH_3	H
X.61	H	H	phenyl	CF_3	CH_3	H
X.62	H	H	phenyl	CF_2H	CH_3	H
X.63	H	H	phenyl	CFH_2	CH_3	H
X.64	H	H	phenyl	CH_3	CH_3	F
X.65	H	H	phenyl	CH_3	CH_3	Cl
X.66	H	H	4-fluorophenyl	CF_3	CH_3	H
X.67	H	H	4-fluorophenyl	CF_2H	CH_3	H

Compound Number	R^1	R^2	R^3	R^4	R^5	R^6
X.68	H	H	4-chlorophenyl	CF_3	CH_3	H
X.69	H	H	4-chlorophenyl	CF_2H	CH_3	H
X.70	H	H	4-bromophenyl	CF_3	CH_3	H
X.71	H	H	4-bromophenyl	CF_2H	CH_3	H
X.72	H	H	2-thienyl	CF_3	CH_3	H
X.73	H	H	3-thienyl	CF_3	CH_3	H
X.74	H	H	2-furyl	CF_3	CH_3	H
X.75	H	H	2-furyl	CF_3	CH_3	H
X.76	H	H	α-methylcyclopropyl	CF_3	CH_3	H
X.77	H	H	α-methylcyclopropyl	CF_2H	CH_3	H
X.78	H	H	α-methylcyclopropyl	CH_3	CH_3	F
X.79	H	H	α-methylcyclopropyl	CH_3	CH_3	Cl
X.80	H	H	α-methylcyclopropyl	CF_3	CH_3	Cl

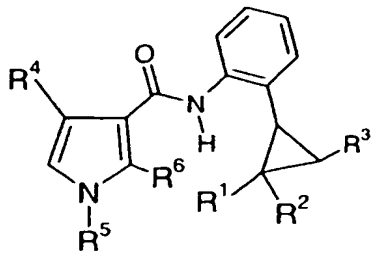
Table 2 provides 80 compounds of formula (1a):



(Ia)

wherein R^1, R^2, R^3, R^4, R^5 and R^6 are as defined in Table 2.

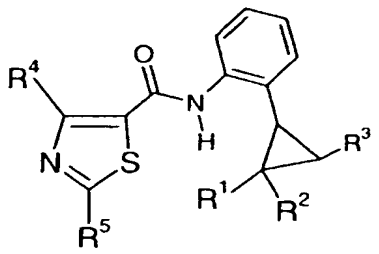
Table 3 provides 80 compounds of formula (1b):



(Ib)

wherein R^1, R^2, R^3, R^4, R^5 and R^6 are as defined in Table 3.

Table 4 provides 50 compounds of formula (1c):



(Ic)

wherein R^1, R^2, R^3, R^4 and R^5 are as defined in Table 4.

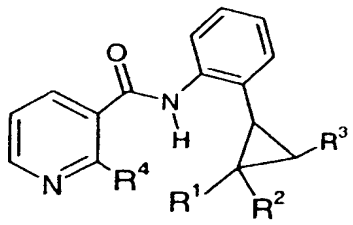
Table 4

Compound Number	R^1	R^2	R^3	R^4	R^5
4.1	H	H	CH_2CH_3	CF_3	CH_3
4.2	H	H	CH_2CH_3	CH_3	CH_3
4.3	H	H	$CH_2CH_2CH_3$	CF_3	CH_3
4.4	H	H	$CH_2CH_2CH_3$	CH_3	CH_3
4.5	H	H	$CH(CH_3)_2$	CF_3	CH_3
4.6	H	H	$CH(CH_3)_2$	CH_3	CH_3
4.7	H	H	$CH(CH_3)_2$	CH_2CH_3	CH_3
4.8	H	H	$CH_2CH_2CH_2CH_3$	CF_3	CH_3
4.9	H	H	$CH_2CH_2CH_2CH_3$	CH_3	CH_3
4.10	H	H	$CH_2CH(CH_3)_2$	CF_3	CH_3
4.11	H	H	$CH_2CH(CH_3)_2$	CH_3	CH_3
4.12	H	H	$C(CH_3)_3$	CF_3	CH_3

Compound Number	R^1	R^2	R^3	R^4	R^5
4.13	H	H	$CH_2CH_2CH_2CH_2CH_3$	CF_3	CH_3
4.14	H	H	$CH_2CH_2CH_2CH_2CH_3$	CH_3	CH_3
4.15	H	H	$CH_2CH_2CH(CH_3)_2$	CF_3	CH_3
4.16	H	H	$CH_2CH_2CH(CH_3)_2$	CH_3	CH_3
4.17	H	H	$CH_2CH_2CH(CH_3)_2$	CH_3	CH_2CH_3
4.18	H	H	$CH_2CH_2CH_2CH_2CH_2CH_3$	CF_3	CH_3
4.19	H	H	$CH_2CH_2CH_2CH_2CH_2CH_3$	CH_3	CH_3
4.20	H	H	cyclopropyl	CF_3	CH_3
4.21	H	H	cyclopropyl	CH_3	CH_3
4.22	H	H	cyclobutyl	CF_3	CH_3
4.23	H	H	cyclobutyl	CH_3	CH_3
4.24	H	H	cyclopentyl	CF_3	CH_3
4.25	H	H	cyclopentyl	CH_3	CH_3
4.26	H	H	cyclohexyl	CF_3	CH_3
4.27	H	H	cyclohexyl	CH_3	CH_3
4.28	H	H	cyclohexyl	CF_3	CH_2CH_3
4.29	H	H	cycloheptyl	CF_3	CH_3
4.30	H	H	cycloheptyl	CH_3	CH_3
4.31	H	H	cycloctyl	CF_3	CH_3
4.32	H	H	cyclooctyl	CH_3	CH_3
4.33	H	H	phenyl	CF_3	CH_3
4.34	H	H	phenyl	CH_3	CH_3
4.35	H	H	4-fluorophenyl	CF_3	CH_3
4.36	H	H	4-fluorophenyl	CH_3	CH_3
4.37	H	H	4-chlorophenyl	CF_3	CH_3
4.38	H	H	4-chlorophenyl	CH_3	CH_3
4.39	H	H	4-bromophenyl	CF_3	CH_3
4.40	H	H	4-bromophenyl	CH_3	CH_3
4.41	H	H	2-thienyl	CF_3	CH_3

Compound Number	R^1	R^2	R^3	R^4	R^5
4.42	H	H	2-thienyl	CH_3	CH_3
4.43	H	H	3-thienyl	CF_3	CH_3
4.44	H	H	3-thienyl	CH_3	CH_3
4.45	H	H	2-furyl	CF_3	CH_3
4.46	H	H	2-furyl	CH_3	CH_3
4.47	H	H	3-furyl	CF_3	CH_3
4.48	H	H	3-furyl	CH_3	CH_3
4.49	H	H	α-methylcyclopropyl	CF_3	CH_3
4.50	H	H	α-methylcyclopropyl	CH_3	CH_3

Table 5 provides 54 compounds of formula (1d):



(Id)

wherein R^1, R^2, R^3 and R^4 are as defined in Table 5.

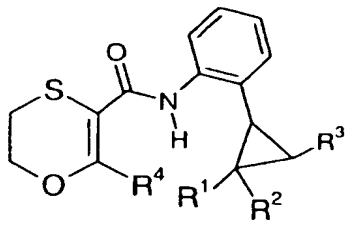
Table 5

Compound Number	R^1	R^2	R^3	R^4
5.1	H	H	CH_2CH_3	Cl
5.2	H	H	$CH_2CH_2CH_3$	Cl
5.3	H	H	$CH_2CH_2CH_3$	Br
5.4	H	H	$CH_2CH_2CH_3$	CF_3
5.5	H	H	$CH(CH_3)_2$	Cl
5.6	H	H	$CH(CH_3)_2$	Br
5.7	H	H	$CH(CH_3)_2$	CF_3
5.8	H	H	$CH_2CH_2CH_2CH_3$	Cl
5.9	H	H	$CH_2CH_2CH_2CH_3$	Br

Compound Number	R^1	R^2	R^3	R^4
5.10	H	H	$CH_2CH_2CH_2CH_3$	CF_3
5.11	H	H	$C(CH_3)_3$	Cl
5.12	H	H	$CH_2CH(CH_3)_2$	Cl
5.13	H	H	$CH_2CH(CH_3)_2$	Br
5.14	H	H	$CH_2CH(CH_3)_2$	CF_3
5.15	H	H	$CH_2CH_2CH_2CH_2CH_3$	Cl
5.16	H	H	$CH_2CH_2CH_2CH_2CH_3$	Br
5.17	H	H	$CH_2CH_2CH(CH_3)_2$	Cl
5.18	H	H	$CH_2CH_2CH(CH_3)_2$	Br
5.19	H	H	$CH_2CH_2CH_2CH_2CH_2CH_3$	Cl
5.20	H	H	$CH_2CH_2CH_2CH_2CH_2CH_3$	Br
5.21	H	H	cyclopropyl	Cl
5.22	H	H	cyclopropyl	Br
5.23	H	H	cyclobutyl	Cl
5.24	H	H	cyclobutyl	Br
5.25	H	H	cyclopentyl	Cl
5.26	H	H	cyclopentyl	Br
5.27	F	F	cyclopentyl	CF_3
5.28	H	H	cyclohexyl	Cl
5.29	H	H	cyclohexyl	Br
5.30	H	H	cyclohexyl	CF_3
5.31	H	H	cycloheptyl	Cl
5.32	H	H	cycloheptyl	Br
5.33	H	H	cycloheptyl	CF_3
5.34	H	H	cyclooctyl	Cl
5.35	H	H	phenyl	Cl
5.36	H	H	phenyl	Br
5.37	H	H	4-fluorophenyl	Cl
5.38	H	H	4-fluorophenyl	Br

Compound Number	R^1	R^2	R^3	R^4
5.39	H	H	4-fluorophenyl	CF_3
5.40	H	H	4-chlorophenyl	Cl
5.41	H	H	4-chlorophenyl	Br
5.42	H	H	4-chlorophenyl	CF_3
5.43	H	H	4-bromophenyl	Cl
5.44	H	H	2-thienyl	Cl
5.45	H	H	2-thienyl	Br
5.46	H	H	3-thienyl	Cl
5.47	H	H	3-thienyl	Cl
5.48	H	H	2-furyl	Cl
5.49	H	H	2-furyl	Br
5.50	H	H	3-furyl	Cl
5.51	H	H	3-furyl	Br
5.52	H	H	2-pyridyl	Cl
5.53	H	H	α-methylcyclopropyl	Cl
5.54	H	H	α-methylcyclopropyl	Br

Table 6 provides 45 compounds of formula (1e):



(1e)

wherein R^1, R^2, R^3 and R^4 are as defined in Table 6.

Table 6

Compound Number	R^1	R^2	R^3	R^4

Compound Number	R^1	R^2	R^3	R^4
6.1	H	H	CH_2CH_3	CH_3
6.2	H	H	$CH_2CH_2CH_3$	CF_3
6.3	H	H	$CH_2CH_2CH_3$	CH_3
6.4	H	H	$CH(CH_3)_2$	CF_3
6.5	H	H	$CH(CH_3)_2$	CH_3
6.6	H	H	$CH_2CH_2CH_2CH_3$	CF_3
6.7	H	H	$CH_2CH_2CH_2CH_3$	CH_3
6.8	H	H	$CH_2CH(CH_3)_2$	CF_3
6.9	H	H	$CH_2CH(CH_3)_2$	CH_3
6.10	H	H	$C(CH_3)_3$	CF_3
6.11	H	H	$C(CH_3)_3$	CH_3
6.12	H	H	$CH_2CH_2CH_2CH_2CH_3$	CF_3
6.13	H	H	$CH_2CH_2CH_2CH_2CH_3$	CH_3
6.14	H	H	$CH_2CH_2CH(CH_3)_2$	CF_3
6.15	H	H	$CH_2CH_2CH(CH_3)_2$	CH_3
6.16	H	H	$CH_2CH_2CH_2CH_2CH_2CH_3$	CF_3
6.17	H	H	$CH_2CH_2CH_2CH_2CH_2CH_3$	CH_3
6.18	H	H	cyclopropyl	CF_3
6.19	H	H	cyclopropyl	CH_3
6.20	H	H	cyclobutyl	CF_3
6.21	H	H	cyclobutyl	CH_3
6.22	H	H	cyclohexyl	CF_3
6.23	H	H	cyclohexyl	CH_3
6.24	H	H	cycloheptyl	CF_3
6.25	F	F	cycloheptyl	CH_3
6.26	H	H	cyclooctyl	CF_3
6.27	H	H	cyclooctyl	CH_3
6.28	F	F	cyclooctyl	CF_3
6.29	H	H	phenyl	CF_3

Compound Number	R^1	R^2	R^3	R^4
6.30	H	H	phenyl	CH_3
6.31	H	H	4-fluorophenyl	CF_3
6.32	H	H	4-flurophenyl	CH_3
6.33	H	H	4-chlorophenyl	CF_3
6.34	H	H	4-chlorophenyl	CH_3
6.35	H	H	4-bromophenyl	CF_3
6.36	H	H	2-thienyl	CF_3
6.37	H	H	2-thienyl	CH_3
6.38	H	H	3-thienyl	CF_3
6.39	H	H	3-thienyl	CH_3
6.40	H	H	2-furyl	CF_3
6.41	H	H	3-furyl	CF_3
6.42	H	H	2-pyridyl	CF_3
6.43	H	H	4-pyridyl	CF_3
6.44	H	H	α-methylcyclopropyl	CF_3
6.45	H	H	α-methylcyclopropyl	CH_3

Throughout this description, temperatures are given in degrees Celsius; "NMR" means nuclear magnetic resonance spectrum; MS stands for mass spectrum; and "%" is percent by weight, unless corresponding concentrations are indicated in other units.

The following abbreviations are used throughout this description:

m.p. = melting point b.p.= boiling point.

S = singlet br = broad

d = doublet dd = doublet of doublets

t = triplet q = quartet

m = multiplet ppm = parts per million

Table 7 shows selected melting point and selected NMR data, all with $CDCl_3$ as the solvent (unless otherwise stated; if a mixture of solvents is present, this is indicated as, for example, ($CDCl_3$ / d_6-DMSO)), (no attempt is made to list all characterising data

in all cases) for compounds of Tables 1 to 6. Unless otherwise stated, the data relate to a cis/trans mixture of each compound; a compound number which ends with the letter 'c' relates only to its cis-isomer and a compound number which ends with the letter 't' relates only to its trans-isomer.

Table 7

Compound Number	^{1}H-NMR data: (ppm/multiplicity/number of Hs).	m.p. / (°C)
1.3	0.6-0.90/m/8H(cis and trans); 1.02/d/6H(cis); 1.11/6H(trans); 1.48/m/1H(trans); 1.78/m/1H(cis); 3.83/s/4H(NH_2 cis and trans); 6.68/m/4H(cis and trans); 7.0/m/4H(cis and trans).	oil
1.5	0.6-1.1/m/6H(cis and trans); 0.95-101/2d/12H(cis and trans); 1.25/m/2H(cis or trans); 1.40/m/2H(cis or trans); 1.78/m/2H(cis or trans); 3.85/s/4H(NH_2 cis and trans); 6.70/m/4H(cis and trans); 7.0/m/4H(cis and trans).	oil
1.6t	0.52/m/1H; 0.80/m/1H; 0.97/s/9H; 1.08/m/1H; 1.57/m/1H; 3.85/s/2H; 6.68/m/2H; 7.0/m/2H.	oil
1.10c	0.01/m/2H, 0.11/m/1H; 0.22/m/1H; 0.58/m/1H; 0.69/m/1H; 0.85/m/1H; 1.67/m/1H; 3.75/s/2H(NH_2); 6.49-6.60/m/2H; 6.82-7.00/m/2H.	oil
1.10t	0.01/m/2H; 0.30/m/2H; 0.55/m/2H; 0.72/m/2H; 1.28/m/1H; 3.70/s/2H(NH_2); 6.45-6.55/m/2H; 6.77-6.85/m/2H.	oil
1.12	0.75/m/4H (cis and trans); 0.97/m/2H (cis and trans); 1.3-1.95/m/20H (cis and trans); 3.88/s/4H (cis and trans); 6.68/m/4H (cis and trans); 7.01/m/4H (cis and trans).	oil
1.13	0.62-1.98/m/30H(cis and trans); 3.80/s/4H(cis and trans); 6.65/m/4H(cis and trans); 6.97/m/4H(cis and trans).	oil
1.17c		110-112
1.17t		69-70
1.18c	1.29/m/1H; 1.52/m/1H; 2.20/m/1H; 2.42/m/1H; 3.55/s/2H; 6.50/d/1H; 6.65-6.85/m/5H; 6.99/t/1H; 7.09/d/1H.	oil

1.18t		95-97
1.22c		60-62
1.22t	0.01-0.1/m/4H; 0.42/m/2H; 0.99/s/3H; 1.01/m/1H; 1.21/m/1H; 3.55/s/2H; 6.45/m/2H; 6.78/m/2H.	oil
2.5		99-102
2.17		75-78
2.18		74-79
2.23		134-136
2.24		110-112
2.33		88-92
2.34c		111-113
2.34t		116-118
2.35c		93-95
2.35t		134-136
2.45	0.6-1.90/m/30H(cis and trans); 4.0/s/6H(cis and trans); 7.0-7.28/m/6H(cis and trans); 8.0/s/1H(trans); 8.05/s/1H(cis); 8.12/d/2H(trans); 8.20/d/2H(cis).	resin
2.46t		116-118
2.52		116-118
2.54		129-131
2.57		107-109
2.66c		resin
2.66t		145-147
2.67c		104-106
2.67t		160-161
2.68c		resin
2.68t		148-150
2.69c		145-147
2.69t		149-150
2.76c		119-121

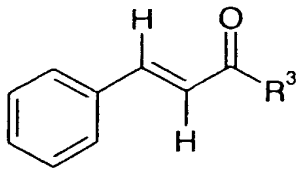
2.76t		107-108
2.77c		82-84
2.77t		109-111
2.78c		119-122
2.78t		96-97
3.5		74-78
3.17		61-65
3.23		92-96
3.33	-0.1-0.90/m/16H(cis and trans); 1.45/m/1H(trans); 1.79/m/1H(cis); 3.58/s/6H (cis and trans); 6.82-7.13/m/10H(cis and trans); 7.92/s/1 (NH-trans); 8.03/dd/1H(trans); 8.10/s/1H(NH-cis); 8.19/dd/1H (cis).	resin
3.39	0.63-1.83/m/26H(cis and trans); 3.72/s/6H(cis and trans); 6.95-7.38/m/10H(cis and trans); 8.05/s/1H(NH-trans); 8.18/dd/1H(trans); 8.30/dd/1H(cis).	resin
3.45	0.6-1.90/m/30H(cis and trans); 3.70/s/6H(cis and trans); 6.98-7.35/m/8H(cis and trans); 8.08/s(broad)/2H(cis and trans); 8.17/d/2H(trans); 8.25/d/2H(cis).	resin
3.66c	1.40/m/1H; 1.50-1.65/m/1H; 2.37/m/1H, 2.50/m/1H; 3.73/s/3H; 6.60-6.70/m/5/H; 6.97/m/2H; 7.18/m/3H; 7.82/s/1H(NH); 8.02/d/1H.	resin
3.66t		146-148
3.68c	1.40/m/1H; 1.57/m/1H; 2.40/m/2H; 3.72/s/3H; 6.68/d/2H; 6.90-7.08/m/4H; 7.18/m/3H; 7.80/s/1H; 8.02/d/1H.	resin
3.68t		150-152
3.76		resin
3.80c		123-126
3.80t		94-96
4.10		69-74
4.12		resin

4.24		113-115
4.26		138-142
5.5		resin
5.12		83-86
5.21c		75-77
5.21t		80-82
5.25		131-133
5.28		115-119
5.37c		164-166
5.37t		133-135
5.40c		160-162
5.40t		136-138
5.53c	-0.25/m/1H; -0.01-0.03/m/3H; 0.60/s/3H; 0.65/m/1H; 0.79/m/1H;1.25/m/1H; 1.80/m/1H; 6.95/t/1H; 7.08/m/2H; 7.28/m/1H; 8.15/d/2H; 8.38/m/1H; 8.62/s/1H(NH).	resin
5.53t	0.01/m/4H; 0.58/m/2H; 0.94/s/3H; 1.11/m/1H; 1.44/m/1H; 6.98/m/2H; 7.09/m/1H; 7.23/m/1H; 8.01/dd/1H; 8.10/d/1H; 8.35/dd/1H; 8.40/s/1H.	resin
6.10		resin

The compounds according to formula (I) may be prepared according to the following reaction schemes.

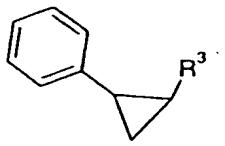
Scheme 1A

A compound of formula (II) [where R^3 is as defined above for a compound of formula (I)] may be prepared by a reaction sequence starting with a crossed-aldol condensation of benzaldehyde with a ketone of formula $CH_3C(O)R^3$ [where R^3 is as defined above for a compound of formula (I)] in the presence of NaOH or KOH in a solvent (such as water or ethanol) and usually under reflux conditions or alternatively by reaction of benzaldehyde with a Wittig reagent under standard conditions. The resulting α,β-unsaturated ketone of formula (III) [where R^3 is as defined above for a compound of formula (I)]:



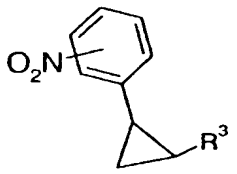
(III)

may then be converted into a compound of formula (IV) [where R^3 is as defined above for a compound of formula (I)]:



(IV)

by reacting first with hydrazine hydrate in ethanol under reflux conditions and then heating (in the range 150 to 250^{0}C) in the presence of KOH (distilling off the solvent). After nitration with HNO_3/H_2O or HNO_3/acetic anhydride in a cooled vessel (in the range -30^{0}C to 0^{0}C), the resultant o/p-mixture of nitrobenzene of formula (V) [where R^3 is as defined above for a compound of formula (I)]:

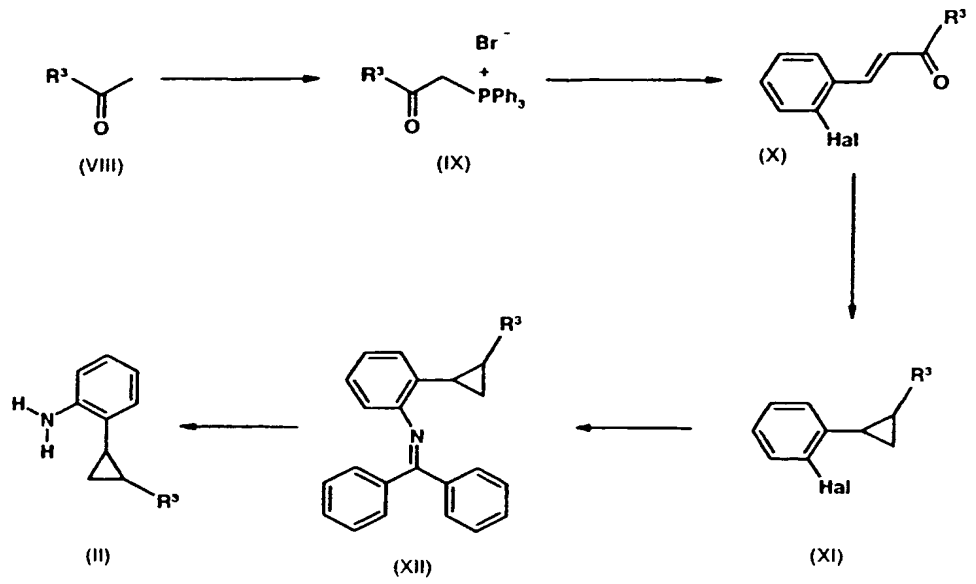


(V)

may then be separated and catalytically reduced ($Pt/C/H_2$ or $Ra\text{-}Ni/H_2$) in a solvent (such as methanol, ethanol or THF) at room temperature, to produce a crude o/p-mixture of a compound of formula (II), which may be further purified by standard techniques.

Alternatively, a compound of formula (II) [where R^3 is as defined above for a compound of formula (I)] may be prepared by a process as illustrated by the following reaction sequence and which involves a Pd(II)-catalysed imination step.

Scheme 1B



A compound of formula (VIII) [where R^3 is as defined above for a compound of formula (I)] is added to bromine and methanol at a temperature of 5-10°C, after which triphenylphosphine in a solvent [such as tetrahydrofuran] is added, to produce a compound of formula (IX) [where R^3 is as defined above for a compound of formula (I)], which in turn is added to sodium hydride, in a solvent [such as DMSO], and then reacted with 2-bromobenzaldehyde or 2-iodobenzaldehyde to yield a compound of formula (X) [where R^3 is as defined above for a compound of formula (I) and Hal is bromo or iodo]. The resultant compound of formula (X) is then mixed with hydrazine hydrate in a solvent [such as ethanol] and heated to reflux, after which potassium hydroxide is added and the resultant reaction mixture is maintained at 200-220°C for several hours. A standard extraction and purification procedure yields a compound of formula (XI) [where R^3 is as defined above for a compound of formula (I) and Hal is bromo or iodo] which may then be converted to a compound of formula (II) by mixing with benzophenone imine, sodium tertiary butoxide, tris-dibenzylideneacetone-dipalladium (Pd_2dba_3), racemic 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) and a solvent [such as benzene or toluene] and heating at reflux temperature, typically for several hours, and adding the resultant [usually crude isolated] imine to a mixture of hydroxylamine hydrochloride, sodium acetate and a solvent [such as methanol]. The resultant mixture is stirred, preferably for about an hour at room temperature, after which

a cis-/trans-mixture of a compound of formula (II) may be extracted and subsequent separation of the cis- and trans-isomers achieved by using flash chromatography.

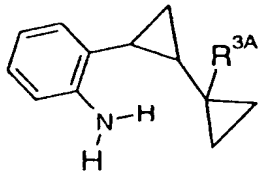
In the above illustrated Pd-catalysed imination process, instead of the catalyst-ligand-system Pd_2dba_3/BINAP, the system palladium diacetate/1,1'-bis(diphenyl-phosphino)ferrocene (dppf) could be used as an alternative.

Reaction scheme 1B is novel and inventive, particularly the use of a Pd(II)-catalysed imination step. Therefore in a still further aspect the present invention provides a process for preparing a compound of formula (II), where R^3 is as defined above, comprising at least one of the steps of reaction scheme 1B; in particular a step using a Pd(II)catalyst-ligand-system [where the ligand is selected from a suitable sterically demanding phosphine (for example BINAP or dppf)] to react a compound of formula (XI) [where Hal is bromo or iodo; and R^3 is as defined above] with benzophenone imine optionally in the presence of a base [such as sodium-*tert*-butanolate, potassium-*tert*-butananolate, sodium carbonate, potassium carbonate or cesium carbonate] to produce a compound of formula (XII) [where R^3 is as defined above].

Examples of imination reactions with benzophenone imine are provided in the literature (Journal of Organometallic Chemistry, 1999, 576, 125-146 and Tetrahedron Letters1997, 38, 6367-6370).

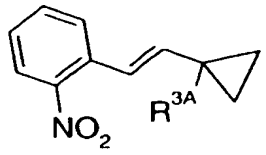
Scheme 2

The synthesis of an amine of formula (IIA)



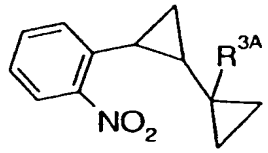
(IIA)

[where R^{3A} is hydrogen or methyl] may be accomplished by a reaction sequence started by a Wittig reaction of o-nitrobenzaldehyde with an ylide [prepared from a cyclopropylmethlytriphenylphosphonium bromide in the presence of a strong base, such as NaH in a solvent such as DMSO, in the range 0-85°C]. The resulting E/Z-mixture of a compound of formula (VI)



(VI)

[where R^{3A} is hydrogen or methyl] may be converted to a compound of formula (VII)



(VII)

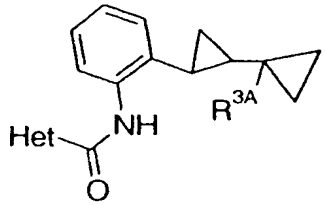
by the application of the Simmons Smith reaction ($Zn/Cu,CH_2I_2$, ether as solvent) to the olefin group of the compound of formula (VI). The reduction of the nitro group of the corresponding compound of formula (VII) may be performed using the conditions described in Scheme 1, to produce a compound of formula (IIA).

Scheme 3

A compound of formula (I) may be prepared by reacting a compound of formula Het-C(=O)-R* [where R* is halogen, hydroxy or C_{1-6} alkoxy, but preferably chloro] with a compound of formula (II) as prepared above in the presence of a base (such as triethylamine, Hunig base, sodium bicarbonate, sodium carbonate, potassium carbonate, pyridine or quinoline, but preferably triethylamine) and in a solvent (such as diethylether, TBME, THF, dichloromethane, chloroform, DMF or NMP) for between 10minutes and 48hours (preferably 12 to 24hours) and between 0°C and reflux (preferably 20 to 25°C). When R* is hydroxy, a coupling agent [such as benzotriazol-1-yloxytris(dimethylamino) phosphoniumhexafluorophosphate, bis-(2-oxo-3-oxazolidinyl)-phosphinic acid chloride, N,N'-dicyclohexylcarbodiimide or 1,1'-carbonyl-diimidazole] may be used.

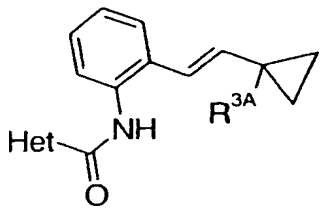
Scheme 4

A compound of formula (IA)



(IA)

[where R^{3A} is hydrogen or methyl] may be prepared by the reduction of the nitro group of a compound of formula (VI) [where R^{3A} is hydrogen or methyl] using standard conditions (for example, catalytic reduction or Béchamp-reduction) followed by amidation with an acid chloride to provide a compound of formula (VII) [where R^{3A} is hydrogen or methyl]



(VII)

which is subsequently used in a Simmons-Smith reaction ($Zn/Cu,CH_2I_2$, ether as solvent) to provide a compound of formula (IA).

Surprisingly, it has now been found that the novel compounds of formula (I) have, for practical purposes, a very advantageous spectrum of activities for protecting plants against diseases that are caused by fungi as well as by bacteria and viruses.

The compounds of formula (I) can be used in the agricultural sector and related fields of use as active ingredients for controlling plant pests. The novel compounds are distinguished by excellent activity at low rates of application, by being well tolerated by plants and by being environmentally safe. They have very useful curative, preventive and systemic properties and are used for protecting numerous cultivated plants. The compounds of formula I can be used to inhibit or destroy the pests that occur on plants or parts of plants (fruit, blossoms, leaves, stems, tubers, roots) of different crops of useful plants, while at the same time protecting also those parts of the plants that grow later e.g. from phytopathogenic microorganisms.

It is also possible to use compounds of formula (I) as dressing agents for the treatment of plant propagation material, in particular of seeds (fruit, tubers, grains) and plant cuttings (e.g. rice), for the protection against fungal infections as well as against phytopathogenic fungi occurring in the soil.

Furthermore the compounds according to present invention may be used for controlling fungi in related areas, for example in the protection of technical materials, including wood and wood related technical products, in food storage, in hygiene management, etc.

The compounds of formula (I) are, for example, effective against the phytopathogenic fungi of the following classes: Fungi imperfecti (e.g. Botrytis, Pyricularia, Helminthosporium, Fusarium, Septoria, Cercospora and Alternaria) and Basidiomycetes (e.g. Rhizoctonia, Hemileia, Puccinia). Additionally, they are also effective against the Ascomycetes classes (e.g. Venturia and Erysiphe, Podosphaera, Monilinia, Uncinula) and of the Oomycetes classes (e.g. Phytophthora, Pythium, Plasmopara). Outstanding activity has been observed against powdery mildew (Erysiphe spp.). Furthermore, the novel compounds of formula I are effective against phytopathogenic bacteria and viruses (e.g. against Xanthomonas spp, Pseudomonas spp, Erwinia amylovora as well as against the tobacco mosaic virus).

Within the scope of present invention, target crops to be protected typically comprise the following species of plants: cereal (wheat, barley, rye, oat, rice, maize, sorghum and related species); beet (sugar beet and fodder beet); pomes, drupes and soft fruit (apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries and blackberries); leguminous plants (beans, lentils, peas, soybeans); oil plants (rape, mustard, poppy, olives, sunflowers, coconut, castor oil plants, cocoa beans, groundnuts); cucumber plants (pumpkins, cucumbers, melons); fibre plants (cotton, flax, hemp, jute); citrus fruit (oranges, lemons, grapefruit, mandarins); vegetables (spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, paprika); lauraceae (avocado, cinnamomum, camphor) or plants such as tobacco, nuts, coffee, eggplants, sugar cane, tea, pepper, vines, hops, bananas and natural rubber plants, as well as ornamentals.

The compounds of formula (I) are used in unmodified form or, preferably, together with the adjuvants conventionally employed in the art of formulation. To this end they are conveniently formulated in known manner to emulsifiable concentrates, coatable pastes, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granulates, and also encapsulations e.g. in polymeric substances. As with the type of the compositions, the methods of application, such as spraying, atomising, dusting, scattering, coating or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances. The compositions may also contain further adjuvants such as stabilizers, antifoams, viscosity regulators, binders or tackifiers as well as fertilizers, micronutrient donors or other formulations for obtaining special effects.

Suitable carriers and adjuvants can be solid or liquid and are substances useful in formulation technology, e.g. natural or regenerated mineral substances, solvents, dispersants, wetting agents, tackifiers, thickeners, binders or fertilizers. Such carriers are for example described in WO 97/33890.

The compounds of formula (I) are normally used in the form of compositions and can be applied to the crop area or plant to be treated, simultaneously or in succession with further compounds. These further compounds can be e.g. fertilizers or micronutrient donors or other preparations which influence the growth of plants. They can also be selective herbicides as well as insecticides, fungicides, bactericides, nematicides, molluscicides or mixtures of several of these preparations, if desired together with further carriers, surfactants or application promoting adjuvants customarily employed in the art of formulation.

The compounds of formula (I) can be mixed with other fungicides, resulting in some cases in unexpected synergistic activities. Mixing components which are particularly preferred are azoles, such as azaconazole, BAY 14120, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazalil, imibenconazole, ipconazole, metconazole, myclobutanil, pefurazoate, penconazole, pyrifenox, prochloraz, propiconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triflumizole, triticonazole; pyrimidinyl carbinole, such as ancymidol, fenarimol, nuarimol; 2-amino-pyrimidines, such as bupirimate, dimethirimol, ethirimol; morpholines, such as dodemorph, fenpropidine, fenpropimorph, spiroxamine, tridemorph; anilinopyrimidines, such as cyprodinil, mepanipyrim, pyrimethanil; pyrroles, such as fenpiclonil, fludioxonil; phenylamides, such as benalaxyl, furalaxyl, metalaxyl, R-metalaxyl, ofurace, oxadixyl; benzimidazoles, such as benomyl, carbendazim, debacarb, fuberidazole, thiabendazole; dicarboximides, such as chlozolinate, dichlozoline, iprodione, myclozoline, procymidone, vinclozoline; carboxamides, such as carboxin, fenfuram, flutolanil, mepronil, oxycarboxin, thifluzamide; guanidines, such as guazatine, dodine, iminoctadine; strobilurines, such as azoxystrobin, kresoxim-methyl, metominostrobin, SSF-129, trifloxystrobin, picoxystrobin, BAS 500F (proposed name pyraclostrobin), BAS 520; dithiocarbamates, such as ferbam, mancozeb, maneb, metiram, propineb, thiram, zineb, ziram; N-

halomethylthiotetrahydrophthalimides, such as captafol, captan, dichlofluanid, fluoromides, folpet, tolyfluanid; Cu-compounds, such as Bordeaux mixture, copper hydroxide, copper oxychloride, copper sulfate, cuprous oxide, mancopper, oxine-copper; nitrophenol-derivatives, such as dinocap, nitrothal-isopropyl; organo-p-derivatives, such as edifenphos, iprobenphos, isoprothiolane, phosdiphen, pyrazophos, tolclofos-methyl; various others, such as acibenzolar-S-methyl, anilazine, benthiavalicarb, blasticidin-S, chinomethionate, chloroneb, chlorothalonil, cyflufenamid, cymoxanil, dichlone, diclomezine, dicloran, diethofencarb, dimethomorph, SYP-LI90 (proposed name: flumorph), dithianon, ethaboxam, etridiazole, famoxadone, fenamidone, fenoxanil, fentin, ferimzone, fluazinam, flusulfamide, fenhexamid, fosetyl-aluminium, hymexazol, iprovalicarb, IKF-916 (cyazofamid), kasugamycin, methasulfocarb, metrafenone, nicobifen, pencycuron, phthalide, polyoxins, probenazole, propamocarb, pyroquilon, quinoxyfen, quintozene, sulfur, triazoxide, tricyclazole, triforine, validamycin, zoxamide (RH7281).

A preferred method of applying a compound of formula (I), or an agrochemical composition which contains at least one of said compounds, is foliar application. The frequency of application and the rate of application will depend on the risk of infestation by the corresponding pathogen. However, the compounds of formula I can also penetrate the plant through the roots via the soil (systemic action) by drenching the locus of the plant with a liquid formulation, or by applying the compounds in solid form to the soil, e.g. in granular form (soil application). In crops of water rice such granulates can be applied to the flooded rice field. The compounds of formula I may also be applied to seeds (coating) by impregnating the seeds or tubers either with a liquid formulation of the fungicide or coating them with a solid formulation.

A formulation [that is, a composition containing the compound of formula (I)] and, if desired, a solid or liquid adjuvant, is prepared in a known manner, typically by intimately mixing and/or grinding the compound with extenders, for example solvents, solid carriers and, optionally, surface active compounds (surfactants).

The agrochemical formulations will usually contain from 0.1 to 99% by weight, preferably from 0.1 to 95% by weight, of the compound of formula I, 99.9 to 1% by weight, preferably 99.8 to 5% by weight, of a solid or liquid adjuvant, and from 0 to 25% by weight, preferably from 0.1 to 25% by weight, of a surfactant.

Advantageous rates of application are normally from 5g to 2kg of active ingredient (a.i.) per hectare (ha), preferably from 10g to 1kg a.i./ha, most preferably from 20g to 600g a.i./ha. When used as seed drenching agent, convenient dosages are from 10mg to 1g of active substance per kg of seeds.

Whereas it is preferred to formulate commercial products as concentrates, the end user will normally use dilute formulations.

The following non-limiting Examples illustrate the above-described invention in more detail.

EXAMPLE 1

This Example illustrates the preparation of Compound No. 1.5.

To a mixture of 17.4g (0.1mol) (2-isobutyl-cyclopropyl)benzene and 80ml of acetic acid anhydride was added a solution of 6.0g (0.095mol) nitric acid and 40ml acetic acid anhydride in such a manner that the internal temperature was kept constant at -30^0C. The resulting reaction mixture was stirred for 1hour at -30^0C and then for 2hours at 0^0C. Then the mixture was poured onto 500ml of ice water and extracted three times with hexane. The hexane phases were combined and twice washed with 5% aqueous bicarbonate solution. After drying of the organic phase over sodium sulphate and distilling off the solvent in a water jet vacuum, the crude reaction product was obtained. Purification by flash chromatography over silica get (eluant: ethylacetate/hexane 1:10) yielded 10.5g of a yellow oil (mixture of para- and ortho-nitroisomers) which was directly used in the next step. This isomeric mixture [consisting of 10.5g (0.048mol) 1-(2-isobutyl-cycloproply)2-nitrobenzene and 1-(2-isobutyl-cyclopropyl)-4-nitrobenzene] was dissolved in 110ml of ethanol and hydrogenated over 5%Pt/C catalyst for 45minutes. After the theoretical uptake of hydrogen had occurred, the catalyst was filtered off and the solvent was removed in vacuo. The crude isomeric aniline mixture was purified by flash chromatography (eluant: ethylacetate/hexane 1:2).

Yield: 6.38g of 2-(2-isobutyl-cyclopropyl)phenyl amine was obtained as a yellow oil (cis/trans mixture).

EXAMPLE 2

This Example illustrates the preparation of Compound 3.17.

A solution of 0.35g (0.0018mol) 1-methyl-4-trifluoromethyl-pyrrole-3-carboxylic acid and 0.24g (0.0019mol) oxalylchloride in 15ml methylenechloride was stirred for

3hours at room temperature in the presence of two drops of absolute DMF. Then the acid chloride solution was slowly added to a solution of 0.34g (0.0018mol) 2-(2-isobutyl-cyclopropyl) phenylamine, 0.27g (0.0027mol) triethylamine and 10ml methylene chloride. The resulting mixture was then stirred for 16hours at room temperature. After removal of the solvent in vacuo, the crude material was taken up in ca. 100ml ethylacetate. The ethylacetate phase was twice washed with water and after drying the organic phase, the solvent was again distilled off in a water jet vacuum. The crude product was purified by flash chromatography (eluant: hexane/ethylacetate/methylene chloride 1:2:2).

Yield: 0.52g 1-methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid [2-(2-isobutyl-cyclopropyl)phenyl]amide in the form of a white powder (cis/trans-mixture).

EXAMPLE 3

This Example illustrates the preparation of Compound Nos. 1.10c and 1.10t.

Step 1:

In a sulfonation flask, NaH (12.8g; 0.32mol) was added to absolute DMSO (600ml). After heating at 80°C for 90minutes, cyclopropylcarbonylmethyltriphenyl phosphoniumbromide (136.5g; 0.32mol) was added portionwise at room temperature. The resultant suspension was stirred for 30minutes at room temperature and then a solution of 2-bromobenzaldehyde (59.4g; 0.32mol) in absolute DMSO (100ml) was added dropwise. After heating the resultant mixture for 4hours at 50°C, the mixture was poured onto 2.5litres of ice water. Extraction with ethylacetate, drying over sodium sulfate and distilling off the solvent in a water jet vacuum yielded the crude product. Purification was achieved by vacuum distillation.

Yield: 77.6g of E-3-(2-bromophenyl)-1-cyclopropylpropenone as a yellow oil (b.p.: 125-130°C at 0.3mbar).

Step 2:

In a sulfonation flask, a mixture of of E-3-(2-bromophenyl)-1-cyclo-propylpropenone (77.6g; 0.309mol) and hydrazine hydrate (23.2g; 0.464mol) in ethanol (25ml) was heated at reflux temperature for 2hours. Then powdered potassium hydroxide (85%) (24.4g; 0.37mol) was added and the excesses of hydrazine hydrate and solvent were distilled out of the flask. The remaining mixture was then heated at a

temperature of 205-210°C for 3hours. The resultant resin was dissolved in ethylacetate (500ml) at a temperature of 50°C and the organic phase was washed twice with water. Drying of the ethylacetate phase over sodium sulfate and distilling off the solvent in a water jet vacuum gave the raw material, which was purified by flash chromatography over silica gel (eluant: hexane/methylene chloride 7:1).

Yield: 61.2g of 2-(2-bromophenyl)bicyclopropyl in the form of a slightly yellowish oil (cis/trans-mixture).

Step 3:

A mixture of 2-(2-bromophenyl)bicyclopropyl (28.5g; 0.12mol), benzophenoneimine (26.1g; 0.144mol), sodium tertiary butoxide (16.1g; 0.168 mol), tris-dibenzyl-ideneacetonedipalladium (Pd_2dba_3) (0.43g; 0.474mmol), racemic 2,2'-bis(diphenylphosphino)1,1'-binaphthyl (BINAP) (0.83g; 1.34mmol) and absolute toluene (450ml) was heated at reflux temperature under an atmosphere of nitrogen for 6hours. Then the solvent was removed in a water jet vacuum and the residue was taken up in ethylacetate (750ml). The organic layer was washed three times with brine and then dried over sodium sulfate. After evaporation of the solvent, the crude product was obtained. Purification was achieved by using flash chromatography over silica gel (eluant: hexane/methylene chloride 5:1).

Yield: 39.9g of cis-/trans-mixture of benzhydrilidene (2-bi-cyclopropyl-2-yl-phenyl)amine in the form of a brownish oil.

Step 4:

In a sulfonation flask, hydroxylamine hydrochloride (0.35g; 0.0048mol), sodium acetate (0.53g; 0.0064mol) and absolute methanol (30ml) were stirred at room temperature for about 15minutes. Then a solution of benzhydrilidene (2-bicyclopropyl-2-yl-phenyl)amine (0.9g; 0.00267 mol) in methanol (15ml) was added dropwise. The resultant mixture was stirred for 1hour at room temperature. After dilution with ethylacetate (250ml), the organic phase was washed twice with water. After drying the organic phase (sodium sulfate) and distilling off the solvent in a water jet vacuum, the crude product was obtained. The final purification and separation of the cis- and trans-isomers was achieved by using flash chromatography (eluant: hexane/ethylacetate 5:1).

Yield: 0.21g of trans- and 0.15g of cis- 2-bicyclopropyl-2-yl-phenylamine in the form of brownish oils.

FORMULATION EXAMPLES FOR COMPOUNDS OF FORMULA (I)

Working procedures for preparing formulations of the compounds of formula I such as Emulsifiable concentrates, Solutions, Granulates, Dusts and Wettable powders are described in WO 97/33890.

BIOLOGICAL EXAMPLES: FUNGICIDAL ACTIONS

Example B-1: Action against *Puccinia recondita* / wheat (Brownrust on wheat)

1 week old wheat plants cv. Arina are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application wheat plants are inoculated by spraying a spore suspension ($1x10^5$uredospores/ml) on the test plants. After an incubation period of 2 days at 20°C and 95% r. h. plants are kept in a greenhouse for 8days at 20°C and 60%r.h. The disease incidence is assessed 10days after inoculation.

Compounds of Tables 2, 3, 4 and 5 show good activity in this test (<20% infestation). Infestation is prevented virtually completely (0-5% infestation) with each of compounds 2.5, 2.17, 2.18, 2.23, 2.24, 2.33, 2.45, 2.46t, 2.76c, 2.76t, 2.77c, 2.77t,3.5, 3.17, 3.23, 3.33, 3.45, 3.76, 4.10, 4.12, 4.26, 5.5, 5.12, 5.21c and 5.37c.

Example B-2: Action against *Podosphaera leucotricha* / apple (Powdery mildew on apple)

5 week old apple seedlings cv. McIntosh are treated with the formulated test compound (0.002% active ingredient) in a spray chamber. One day after application apple plants are inoculated by shaking plants infected with apple powdery mildew above the test plants. After an incubation period of 12 days at 22°C and 60%r.h. under a light regime of 14/10hours (light/dark) the disease incidence is assessed.

Compounds of Tables 2, 3 and 4 show good activity in this test. The compounds 2.5, 2.17, 2.18, 2.23, 2.24, 2.33, 2.45, 2.46t, 3.5, 3.17, 3.23, 3.33, 3.45, 4.10 and 4.12 each exhibit strong efficacy (<20% infestation).

Example B-3: Action against *Venturia inaequalis* / apple (Scab on apple)

4 week old apple seedlings cv. McIntosh are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application apple plants are inoculated by spraying a spore suspension ($4x10^5$conidia/ml) on the test plants. After an incubation period of 4 days at 21°C and 95%r.h. the plants are placed for 4 days at 21°C and 60%r.h. in a greenhouse. After another 4 day incubation period at 21°C and 95%r.h. the disease incidence is assessed.

Compounds of Tables 2 and 3 show good activity in this test. The compounds 2.5, 2.17, 2.18, 2.23, 2.24, 2.33, 2.45, 2.46t, 3.5, 3.17, 3.23, 3.33 and 3.45 each exhibit strong efficacy (<20% infestation).

Example B-4: Action against *Erysiphe graminis* / barley (Powdery mildew on barley)

1 week old barley plants cv. Express are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application barley plants are inoculated by shaking powdery mildew infected plants above the test plants. After an incubation period of 6 days at 20°C / 18°C (day/night) and 60%r. h. in a greenhouse the disease incidence is assessed.

Compounds of Tables 2, 3 and 4 show good activity in this test. The compounds 2.5, 2.17, 2.18, 2.23, 2.24, 2.45, 2.46t, 2.77c, 2.77t, 3.5, 3.17, 3.23, 3.45, 4.10 and 4.12 each exhibit strong efficacy (<20% infestation).

Example B-5: Action against *Botrytis cinerea* / apple (Botrytis on apple fruits)

In an apple fruit cv. Golden Delicious 3 holes are drilled and each filled with 30µl droplets of the formulated test compound (0.002% active ingredient). Two hours after application 50 µl of a spore suspension of *B. cinerea* ($4x10^5$conidia/ml) are pipetted on the application sites. After an incubation period of 7 days at 22°C in a growth chamber the disease incidence is assessed.

Compounds of Tables 2, 3, 4, 5 and 6 show good activity in this test. The compounds 2.5, 2.17, 2.18, 2.23, 2.24, 2.33, 2.45, 2.46t, 2.76c, 2.76t, 2.77c, 2.77t, 3.5, 3.17, 3.23, 3.33, 3.76, 3.45, 3.76, 4.10, 4.12, 4.26, 5.5, 5.12, 5.21c and 5.37 each exhibit very strong efficacy (<10% infestation).

Example B-6: Action against *Botrytis cinerea* / grape (Botrytis on grapes)

5 week old grape seedlings cv. Gutedel are treated with the formulated test compound (0.002% active ingredient) in a spray chamber. Two days after application

grape plants are inoculated by spraying a spore suspension ($1x10^6$ conidia/ml) on the test plants. After an incubation period of 4 days at 21°C and 95%r.h. in a greenhouse the disease incidence is assessed.

Compounds of Tables 2, 3, 4, 5 and 6 show good activity in this test. The compounds 2.5, 2.17, 2.18, 2.23, 2.24, 2.45, 2.46t, 2.76c, 2.76t, 2.77c, 2.77t, 3.5, 3.17, 3.23, 3.33, 3.39, 3.76, 4.10, 4.12, 4.26, 5.5, 5.12, 5.21c and 5.37c each exhibit very strong efficacy (<10% infestation).

Example B-7: Action against *Botrytis cinerea* / tomato (Botrytis on tomatoes)

4 week old tomato plants cv. Roter Gnom are treated with the formulated test compound (0.002% active ingredient) in a spray chamber. Two days after application tomato plants are inoculated by spraying a spore suspension ($1x10^5$conidia/ml) on the test plants. After an incubation period of 4 days at 20°C and 95%r.h. in a growth chamber the disease incidence is assessed.

Compounds of Tables 2, 3, 4, 5 and 6 show good activity in this test. The compounds 2.5, 2.17, 2.18, 2.23, 2.24, 2.33, 2.45, 2.46t, 2.76c, 2.76t, 2.77c, 2.77t, 3.5, 3.17, 3.23, 3.39, 3.45, 3.76, 4.10, 4.12, 4.26, 5.5, 5.12, 5.21c and 5.37c each exhibit very strong efficacy (<10% infestation).

Example B-8: Action against *Pyrenophora teres* / barley (Net blotch on barley)

1 week old barley plants cv. Express are treated with the formulated test compound (0.002% active ingredient) in a spray chamber. Two days after application barley plants are inoculated by spraying a spore suspension ($3x10^4$conidia/ml) on the test plants. After an incubation period of 2 days at 20°C and 95%r.h. plants are kept for 2 days at 20°C and 60%r.h. in a greenhouse. The disease incidence is assessed 4 days after inoculation.

Compounds of Tables 2, 3, 4, 5 and 6 show good activity in this test. The compounds 2.5, 2.17, 2.18, 2.23, 2.24, 2.33, 2.45, 2.46t, 2.76c, 2.76t, 2.77c, 2.77t, 3.5, 3.17, 3.23, 3.39, 3.45, 3.76, 4.10, 4.12, 4.26, 5.5, 5.12, 5.21c and 5.37c each exhibit very strong efficacy (<20% infestation).

Example B-9: Action against *Septoria nodorum* / wheat (Septoria leaf spot on wheat)

1 week old wheat plants cv. Arina are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application wheat plants are inoculated by spraying a spore suspension ($5x10^5$conidia/ml) on the test plants. After an

incubation period of 1 day at 20°C and 95%r.h. plants are kept for 10 days at 20°C and 60%r.h. in a greenhouse. The disease incidence is assessed 11 days after inoculation.

Compounds of Tables 2, 3 and 4 show good activity in this test. The compounds 2.5, 2.17, 2.18, 2.23, 2.24, 2.33, 2.45, 2.46t, 2.76c, 2.76t, 2.77c, 2.77t, 3.5, 3.17, 3.23, 3.33, 3.39, 3.45, 3.76, 4.10 and 4.12 each exhibit strong efficacy (<20% infestation).